

Self-Diffusion of Gold*

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The self-diffusion of gold was measured in single crystalline specimens of 99.8 and 99.999% purity in the temperature range from 600–954°C, by using Au¹⁹⁸ as tracer and applying the sectioning technique. The temperature dependence of the self-diffusion coefficient is given by

$$D = (0.031 \pm 0.004) \exp[-(39\,360 \pm 280)/RT] \text{ cm}^2/\text{sec.}$$

Together with recently reported data on self-diffusion of copper, silver, and lead, this result is compared with empirical and theoretical predictions.

INTRODUCTION

IN the last decade, much effort has been given to developing accurate techniques for measurement of diffusion in metals. Generally speaking, the sectioning technique seems to give the most reliable results. It seemed worthwhile to measure the self-diffusion of gold by the same technique, because there is a serious discrepancy between the values already obtained by different authors,^{1–4} only one of whom used a sectioning method. In the present investigation, the self-diffusion of gold was measured between 600 and 954°C in single crystalline specimens of 99.8 and 99.999% purity, using Au¹⁹⁸ as a tracer and applying the sectioning technique. It is also of interest to compare the self-diffusion of gold with the self-diffusion of copper, silver, and lead for which very accurate data are now available.^{5–8} Comparison of experimental self-diffusion data for different metals with predictions made by theories may contribute toward a better understanding of the diffusion process.

EXPERIMENTAL

Single crystals (approximately 10 cm long and 1.2 cm diameter) were grown from the melt in high-purity graphite crucibles in a vacuum furnace, following the method described by Lazarus and Chipman.⁹ The crystals were etched with KCN(NH₄)₂S₂O₈. The orientation was obtained from standard Laue back-reflection diagrams.

The crystal was then embedded in plaster of Paris and cut into cylinders of 6–8 mm thickness with a

jeweler's saw. The flat surfaces of the cylinders were carefully machined and made plane parallel on a precision lathe, as described for lead in reference 8. By taking successively thinner cuts up to 5 microns, the deformed layer was easily removed by annealing the specimen at 950°C for 10 days in vacuum. The annealed specimens were etched to make sure no grains were present. The condition of the flat surface was tested with the Laue back reflection technique; after the annealing, the Laue spots did not show asterism. From several specimens the orientation of the flat surface was obtained; in all cases this orientation was in agreement with the orientation of the original crystal.

The Au isotope was received from the Oak Ridge National Laboratory in the form of gold foil with a specific activity of 3 curies/gram. The gold was dissolved in aqua regia and the resulting solution was diluted and neutralized. Then KCN and Na₂HPO₄ · 12H₂O were added according to a recipe given by Blum and Hogaboom.¹⁰ The specimens were electroplated by using a gold or platinum electrode; the current density was 3–5 ma/cm². It is estimated that the plated layer was less than 200 Å thick.

The plated specimens were sealed off in evacuated vycor tubing and placed inside a massive nichrome block in diffusion furnaces with controlled temperatures as described previously by Tomizuka and Slifkin.¹¹ The temperature was measured with a platinum-platinum-rhodium thermocouple. The inaccuracy in the quoted temperatures, due to thermal fluctuations and errors in calibration, is of the order of 1.5°C, resulting in an inaccuracy in the diffusion coefficient of the order of 3%. The diffusion-time was chosen to give a measurable penetration depth of about 250 microns; however, because of the relatively short half-life of the isotope (2.7 days), this time was never longer than 4 weeks.

After the diffusion annealing, the specimen was sectioned on a precision lathe into layers of 12 or 25 microns thickness, after removal of about 1.5 mm of

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³ H. C. Gatos and A. Azzam, *J. Metals* **4**, 407 (1952).

⁴ H. C. Gatos and A. D. Kurtz, *J. Metals* **6**, 616 (1954).

⁵ Kuper, Letaw, Slifkin, Sonder, and Tomizuka, *Phys. Rev.* **96**, 1224 (1954); **98**, 1870 (1955).

⁶ C. T. Tomizuka and E. Sonder, *Phys. Rev.* **103**, 1182 (1956), this issue.

⁷ N. H. Nachtrieb and G. S. Handler, *J. Chem. Phys.* **23**, 1569 (1955).

⁸ B. Okkerse, thesis, Delft, The Netherlands, 1954 (to be published).

⁹ D. Lazarus and D. R. Chipman, *Rev. Sci. Instr.* **22**, 211 (1951).

¹⁰ W. Blum and G. B. Hogaboom, *Principles of Electroplating and Electroforming* (McGraw-Hill Book Company, Inc., New York, 1949), p. 302.

¹¹ C. T. Tomizuka and L. Slifkin, *Phys. Rev.* **96**, 610 (1954).

TABLE I. Experimental data.

Experiment No.	Diffusion temperature °C	1000/T (°K) ⁻¹	Diffusion time sec	D cm ² /sec	Counting technique ^a	Purity of sample %	Probable error % ^b	Deviation from Eq. (1) %
1	600	1.1455	2.313×10 ⁶	4.26×10 ⁻¹²	d	99.8	0.42	-0.5
24	603	1.1416	1.634×10 ⁶	4.60×10 ⁻¹²	d	99.999	0.56	-0.4
20	642	1.0929	1.621×10 ⁶	1.11×10 ⁻¹¹	d	99.999	1.34	-9.0
2	650	1.0834	1.186×10 ⁶	1.60×10 ⁻¹¹	d	99.8	1.90	+8.7
9	702	1.0256	1.358×10 ⁶	4.49×10 ⁻¹¹	d	99.8	0.52	-2.4
21a	716	1.0111	9.225×10 ⁵	6.83×10 ⁻¹¹	d	99.999	0.92	+10.2
21b	716	1.0111	9.225×10 ⁵	6.78×10 ⁻¹¹	s	99.999	0.97	+9.6
3	722	1.0050	6.666×10 ⁵	6.52×10 ⁻¹¹	d	99.8	0.61	-6.1
4	756	0.9718	3.372×10 ⁵	1.37×10 ⁻¹⁰	d	99.8	0.55	+2.2
8	806	0.9268	1.716×10 ⁵	3.14×10 ⁻¹⁰	d	99.8	0.41	-3.8
23a	829	0.9074	2.140×10 ⁵	4.63×10 ⁻¹⁰	d	99.999	3.61	-3.2
23b	829	0.9074	2.140×10 ⁵	4.77×10 ⁻¹⁰	s	99.999	0.95	-0.2
30	847	0.8933	8.766×10 ⁴	6.24×10 ⁻¹⁰	d	99.8	1.33	-1.3
22a	903	0.8504	6.060×10 ⁴	1.50×10 ⁻⁹	d	99.999	0.65	+1.3
22b	903	0.8504	6.060×10 ⁴	1.54×10 ⁻⁹	s	99.999	1.09	+3.9
5	904	0.8496	2.478×10 ⁴	1.54×10 ⁻⁹	d	99.8	0.63	+2.6
7	954	0.8150	1.044×10 ⁴	2.90×10 ⁻⁹	d	99.8	1.08	-2.8

^a d = dry-counted, s = solution counted.^b Based on least squares calculation.

material from the outer surface. The chips were collected and dry-counted with an end-window counter in the same manner as described for lead.⁸ Some specimens were immersion-counted as well, as described in reference 11, in order to compare the reliability of the dry-counting technique. The measured intensities were corrected for background, deadtime of the counter, and radioactive decay.

From the corrected intensity and the weight of each layer, the diffusion coefficient was computed. For each point of the penetration curve the inaccuracy in the concentration is about 1.5%, and the inaccuracy in the distance is about 1%.

All crystals were grown from gold of 99.8% purity ("0.998 fine"), except in one case in which gold of 99.999% purity was used.

RESULTS

In all experiments a linear relationship was found between the logarithm of the concentration and the square of the penetration depth. The conditions and the results of all experiments are given in Table I.

In Fig. 1 the logarithm of the diffusion coefficient is plotted as a function of the reciprocal absolute temperature.

The temperature dependence of the diffusion coefficient is given by the relation

$$D = (0.031 \pm 0.004) \exp[-(39360 \pm 280)/RT] \text{ cm}^2/\text{sec}, \quad (1)$$

in which the errors are the probable errors as found from a least squares calculation based on the data given in Table I. These probable errors are of the order of 1%. Together with the uncertainty in the temperature of the diffusion annealing, these errors can account for an inaccuracy in each diffusion coefficient of about 4%. The average direction of each experimental point from

relation (1) is 4.0%. The average deviation of each experimental point from this relation is 4.0%.

DISCUSSION

Analyzing the data, one observes that the three experiments, in which the chips were counted in two different ways, show that, in this investigation, the dry-counting technique is as accurate as the immersion-counting technique: the average deviations from the straight line in Fig. 1 are, respectively, 4.9 and 4.6%.

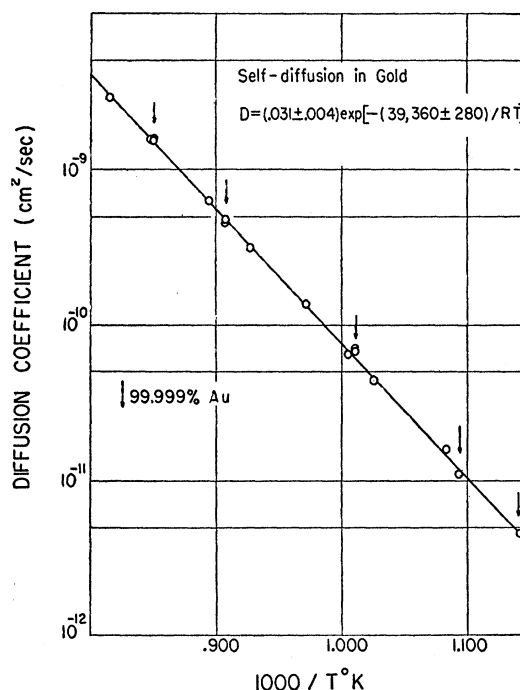


FIG. 1. Temperature dependence of the self-diffusion coefficient of gold.

TABLE II. Reported self-diffusion data of gold.

	D_0 , cm ² /sec	Q , kcal/mole
Sagursky ^a	0.16	53.0
McKay ^b	0.02	51.0
Gatos and Kurtz ^c	0.265	45.3
Present work	0.031±0.004	39.4±0.3

^a See reference 1.^b See reference 2.^c See reference 4.

Under certain conditions (depending on the nature of the material, the emitted radiation and the counting equipment) the dry-counting technique can be a valuable short cut compared to the more elaborate immersion-counting technique (see for instance reference 8).

Within the accuracy of the experiments, there appears to be no difference between the rate of self-diffusion in specimens of 99.8 and 99.999% purity. The average deviation of the "very pure points" from the straight line in Fig. 1, taking signs into account, is 0.3%; the positive and negative deviations are randomly distributed over the entire temperature range.

The present investigation results in an activation energy of 39 360 cal/mole and a frequency factor of 0.031 cm²/sec. Both values differ severely from the most recently reported values (see Table II), which were obtained by Gatos and Kurtz⁴ by means of an autoradiographic technique. Over the entire temperature range the diffusion coefficients found by these authors are smaller than the coefficients calculated from Eq. (1), the difference being larger for low temperatures. The reason for this discrepancy is not known; however, the scatter in the previous experimental results is worse than in the present investigation (on the average 12% and 4.0%, respectively). It should be observed that within the experimental error, the activation energy is in agreement with the results obtained by Kauffman and Koehler,¹² who calculated the activation energy from resistivity changes in quenched gold that was subsequently annealed.† The value for the activation energy is lower than one would expect on the basis of empirical rules, which relate the activation energy of self-diffusion in metals to the latent heat of melting, the melting point, or the heat of sublimation.

It is of interest to compare the present data, together with other recently reported values for self-diffusion in face-centered cubic metals (all obtained by using the sectioning technique), with predictions made by theoretical treatments on this subject. Various authors have, on the basis of thermodynamic arguments, related the D_0 and Q to other physical constants. For the

case of self-diffusion in face-centered cubic metals, assuming the vacancy-mechanism, these theories may be stated as follows. Zener¹³ suggested that the frequency factor may be written as

$$D_0 = a^2 \nu \exp(\Delta S/R),$$

in which a is the lattice constant, ν the Debye frequency, and ΔS the entropy change. He then assumes that a fraction λ of the activation-energy Q goes into straining the lattice elastically, and shows that the entropy change can be written as

$$\Delta S = \lambda \beta Q/T_m,$$

in which β is a constant proportional to the temperature dependence of the shear modulus and T_m the melting point. From experimental data Zener calculated λ , and he found that this λ is reasonably constant for several f.c.c. metals, the average value being 0.55. Based on the presumably more accurate data available now, we find the average value of λ to be 0.45 (see Table III).

Le Claire¹⁴ expanded Zener's theory and assumed that the enthalpy required to form a vacancy is proportional to the heat of sublimation Q_s :

$$\Delta H_1 = k_1 Q_s.$$

He also assumed that the free energy of motion results from elastic strains which are localized in a volume proportional to the atomic volume

$$\Delta F_2 = k_2 \mu (M/\rho),$$

in which μ is the shear modulus, M the atomic weight, and ρ the density. It is assumed that k_1 and k_2 are constants for metals with the same structure. It is then possible to relate these constants to the experimental values for D_0 and Q . Using older data, Le Claire found that k_1 and k_2 are reasonably constant, the average values being respectively 0.215 and 0.215. Based on the data available now, we find 0.26 and 0.16, as shown in Table III.

Another attempt to correlate diffusion data on the basis of Zener's derivation was made by Buffington and Cohen.¹⁵ These authors calculated the elastic work done by the diffusing atom and related this energy to the total activation energy for diffusion. They derived the expression

$$Q = KE_0 a_0^3,$$

in which E_0 is the Young's modulus and a_0 the lattice parameter, both at 0°K. As Zener did, they assumed that a fraction λ_D of Q is needed for straining the lattice. They derive the expression

$$D_0 = a^2 \nu \exp[\lambda_D KE_0 a_0^3 (\varphi - 3\alpha)/R],$$

in which φ is the temperature dependence of E and α

¹² J. W. Kauffman and J. S. Koehler, Phys. Rev. **88**, 149 (1952); **97**, 555 (1955). See also F. Seitz and J. S. Koehler in *Solid State Physics* (Academic Press, Inc., New York, 1956), Vol. 2, p. 397.

† Note added in proof.—The present value for the activation energy is in excellent agreement with the results of quenching experiments, recently published by Bauerle, Klabande, and Koehler, Phys. Rev. **102**, 1182 (1956).

¹³ C. Zener, J. Appl. Phys. **22**, 372 (1951).

¹⁴ A. D. Le Claire, Acta Metallurgica **1**, 438 (1953).

¹⁵ F. S. Buffington and M. Cohen, Acta Metallurgica **2**, 660 (1954).

TABLE III. Comparison of recent self-diffusion data of f.c.c. metals with theoretical treatments.

		Cu Kuper <i>et al.</i> ^a	Sectioning technique Ag Tomizuka <i>et al.</i> ^b	Au Present work	Pb Nachtrieb <i>et al.</i> ^c	Pb Okkerse ^d	Average	Autoradiographic technique Au Gatos <i>et al.</i> ^e
	D_0 in cm ² /sec	0.20±0.03	0.40±0.04	0.031±0.004	0.28	0.74±0.45		0.27
	Q in kcal/mole	47.1±0.3	44.1±0.2	39.4±0.3	24.2±0.8	25.3±0.5		45.3
	Q/Q_0	59	65	44	52	55		51
	Q/Q_m	15.2	16.1	12.9	20.4	21.3		14.9
	Q/T_m	35	36	30	40	42		34
Zener ^f	λ	0.51	0.49	0.35	0.41	0.48	0.45	0.71
Le Claire ^g	k_1	0.22	0.27	0.25	0.29	0.26	0.26	0.05
	k_2	0.16	0.18	0.12	0.15	0.17	0.16	0.16
Buffington and Cohen ^h	K	0.049	0.050	0.045	0.046	0.048	0.047	0.052
	λ_D	0.60	0.57	0.36	0.44	0.52	0.50	0.73

^a See reference 5.^b See reference 6.^c See reference 7.^d See reference 8.^e See reference 4.^f See reference 13.^g See reference 14.^h See reference 15.

the coefficient of thermal expansion. Again, they found the constants K and λ_D reasonably well constant for different metals, the average values being 0.0514 and 0.64, respectively. From the data available now, these values appear to be 0.047 and 0.50 (see Table III). It should be noted that Zener's λ and Buffington-Cohen's λ_D are calculated in essentially the same way, the difference being in the choice of the elastic modulus whose temperature derivative enters into the expression. It is then no surprise that these constants turn out to be about the same, namely 0.45 and 0.50. This value would indicate that approximately 50% of the activation energy is elastic energy, associated with the formation and motion of the defects. Nachtrieb and Handler¹⁶ proposed a mechanism for diffusion, in which the elementary diffusion act takes place in a small liquid-like region of disorder, in which a vacancy is distributed. They found support for this assumption in the empirical

rule that the activation energy is proportional to the heat of melting, Q_m ; older data suggested

$$Q = 16.5Q_m.$$

From Table III it appears that this rule is not justified.

Upon surveying the available data, it appears to be very difficult to say which theoretical relation offers the best approach to the understanding of metallic diffusion. Moreover, the scatter of the different constants appears to be larger than originally computed on the basis of older diffusion data.

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¹⁶ N. H. Nachtrieb and G. S. Handler, *Acta Metallurgica* **2**, 797 (1954).